Resonant Magnetization Tunneling in Mn_{12} Acetate: The Absence of Inhomogeneous Hyperfine Broadening

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We present the results of a detailed study of the thermally-assisted-resonant-tunneling relaxation rate of Mn_{12} acetate as a function of an external, longitudinal magnetic field and find that the data can be fit extremely well to a Lorentzian function. No hint of inhomogeneous broadening is found, even though some is expected from the Mn nuclear hyperfine interaction. This inconsistency implies that the tunneling mechanism cannot be described simply in terms of a random hyperfine field.

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The molecular magnet Mn_{12} acetate, with spin 10 and large uniaxial anisotropy, has garnered much attention since its hysteresis loop was found to exhibit steps at regular intervals of magnetic field [1]. This phenomenon, now confirmed by other experiments on this [2–6] and other materials [7–10], has been interpreted as a manifestation of resonant tunneling of the magnetization, first suggested to occur in this system in Refs. 11 and 12. The system is modeled as a double-well potential (Fig. 1) with energy levels that correspond to the different projections of the spin along the easy axis. An external magnetic field will tilt the potential. At specific values of field, levels in opposite wells come into resonance and thermally assisted tunneling between the wells becomes possible (solid arrows in Fig. 1), increasing the interwell relaxation rate and thereby producing steps in the hysteresis loops. The dashed arrows in Fig. 1 schematically illustrate the nonresonant process of simple thermal activation over the classical energy barrier (which in some cases may differ from the full barrier shown [13]).

Mn_{12} acetate has been quantitatively described [1,3,14] by the Hamiltonian:

$$\mathcal{H} = -DS_z^2 - g\mu_B H_z S_z + \mathcal{H}' \tag{1}$$

where $D \approx 0.6K$ represents the anisotropy energy that breaks the 21-fold zero-field Zeeman degeneracy and $\mathcal{H}'$ is a perturbation that does not commute with S_z. (Recent EPR experiments [15,16] have indicated the presence of additional terms in the Hamiltonian that are fourth order in the spin operators.) In the absence of a symmetry-breaking term, $\mathcal{H}'$, S_z is conserved and hence no tunneling is allowed between levels. The symmetry of $\mathcal{H}'$ determines a selection rule that governs which level crossings may give rise to tunneling. Many early theoretical treatments [17–19] of tunneling in spin systems focused on a transverse anisotropy of the form kS_x^2, which leads to a selection rule $\Delta m = 2i$ for integer i. It was then somewhat surprising that this selection rule was violated [1,3,20] in the case of Mn_{12}. That is, the rule implies that every other step should be missing. In fact, all steps are observed and there is no discernible difference between steps that obey the selection rule and those that violate it. This prompted the suggestion [20,21] that the tunneling must instead be produced by a transverse magnetic field, $\mathcal{H}' = g\mu_B S_x H_T$, which imposes no selection rule. Since no such field was applied externally in the experiments, it was concluded that the transverse component of an internal field of dipolar or hyperfine origin may be responsible [20]. Dipolar fields have now largely been ruled out by recent experiments [22]. On the other hand, hyperfine fields within a Mn_{12} cluster have been estimated to be on the order of a few hundred Oe [23] and estimates [13,20,24] have shown that this is sufficient for tunneling to occur between levels near the top of the energy barrier, allowing the thermally assisted tunneling process illustrated in Fig. 1.

Much recent theoretical activity [21,25–32] has focused on determining the details of the relaxation process. Many of these studies predict a resonance width that is much narrower than that observed, a discrepancy that has been addressed by assuming that the resonances are inhomogeneously broadened [21,26,27,30] by dipolar or hyperfine fields or by misalignment of the crystallites in oriented-powder samples. In this report, we present the results of detailed measurements of the relaxation rate as a function of magnetic field in the neighborhood of a resonance. We find that

the data can be fit with high fidelity to a Lorentzian function and show no hint of inhomogeneous broadening. The linewidth corresponds to a time scale that does not match any relevant microscopic time known for the system. We suggest that it may represent a hitherto unrecognized component of the relaxation process.

A powder of Mn_{12} prepared according to [33] was oriented in a 5.5 Tesla field and set in a paraffin matrix in a manner similar to the procedure described in Refs. 1 and 20. Hysteresis loops for this sample were published in reference 20; the squareness of the loops indicates the crystallites were well oriented. Measurements were performed with a Quantum Design MPMS-5 magnetometer; the superconducting magnet was quenched prior to taking data to eliminate any remanent field. We estimate the misalignment of a typical crystallite to be ≈ 1 degree. For the largest magnetic field of 500 Oe applied in the present study, this misalignment corresponds to a maximum unintentional transverse field of ≈ 9 Oe, a value much too small to have any effect on the tunneling, which is thought to be produced by a transverse field of several hundred Oersteds.

Measurements were performed as follows. The sample was cooled in zero field from 5 K (where the sample is superparamagnetic) to below the blocking temperature of 3 K. After allowing the system to thermally stabilize, a magnetic field was applied and the magnetization was measured as a function of time to obtain its relaxation rate. We note [20,34] that the field experienced by a molecular cluster is the superposition of the externally applied field and the internal mean dipolar field produced by the other clusters. Compared with measuring the relaxation from a finite magnetization toward M ≈ 0, the above procedure provides the advantage that the internal field associated with the change in the sample magnetization changes little compared to the externally applied field, so that the total field is almost constant.

A typical relaxation curve is shown on a semilogarithmic scale in the inset to Fig. 2. As noted in several previous publications [1,20,35,36], the single-exponential relaxation expected for a sample ostensibly comprising identical molecules is not observed. We suggest that this may be due to slight variations in the local environment of the clusters, perhaps related to the number of proximal molecules of solvation. To eliminate the effect of such variations, we measured the longest relaxation time by fitting the long-time tail of the relaxation to a single exponential, as shown in the inset to Fig. 2. The high quality of the fit indicates that all faster processes have died out. The relaxation rate obtained this way at 2.6 K is plotted as a function of applied field in the main part of Fig. 2. [37] The qualitative signature of resonant tunneling is apparent: when the field increases from zero, the relaxation rate decreases as matching levels in opposite wells become detuned. The figure also shows the results of fitting the data to a Lorentzian and to a Gaussian, each superimposed on a background of the form $\Gamma_{nonres} Cosh(g\mu_B SH/k_B T)$, which represents the non-resonant, over-barrier part of the relaxation. [38] The Lorentzian fit is excellent while the Gaussian fit clearly is not, failing especially in the tails.

On a semilogarithmic scale, Fig. 3 shows data taken at four different temperatures, as indicated. A Lorentzian fit is applied to each set. From these fits the full width is found to be $267, 236, 270$ and 271 Oe for 2.5, 2.6, 2.7 and 2.8 K, respectively. This is consistent with the width found by fitting ac susceptibility data to a Lorentzian [6]. The present experiments were limited to a small temperature range in which a large portion of the relaxation could be measured in a reasonable time. Because of this limitation, the effective energy barrier (an Arrhenius plot) could not be deduced from the data, as has been done in ac measurements [6,12,39]. However, one can get a crude estimate of the difference in the height of the energy barrier on resonance and off resonance if one assumes that in both cases the relaxation obeys an Arrhenius law, $\Gamma = \omega_0 e^{-U/kT}$, with a prefactor ω_0 that is approximately independent of field. Then, the change in the effective energy barrier, ΔU, is given by $\Delta U = Tln(\Gamma(H=0)/\Gamma_{nonres})$. The fits then yield $\Delta U = 3.58, 4.73, 5.00$ and 5.40 K for $T = 2.5, 2.6, 2.7$ and 2.8 K, respectively.

The absence of any apparent inhomogeneous broadening of the resonance is quite unexpected. Since all resonances appear to have the same height, [1,3,20] the tunneling must in large part be driven by a transverse magnetic field of at least a few hundred Oe. [20] The most likely source for such a field is the Mn nuclear spins. This has been estimated [23] to be $300 - 500$ Oe. We stress that even were the hyperfine fields to play no role in the tunneling, their presence is nevertheless expected and should give rise to inhomogeneous broadening of the resonance. Luis et al. [6] have suggested that the broadening they observe is due at least in part to interactions with hyperfine and dipole fields. We note, however, that such interactions should give rise to a Gaussian lineshape. It is puzzling that no such broadening is observed.

There are now numerous theories of relaxation in Mn_{12}, but none are able to provide accurate, quantitative descriptions of the resonance lineshape and linewidth. Dobrovitski and Zvezdin [27] have considered a model of tunneling out of the ground state that predicts a resonance width several orders of magnitude lower than that observed. They suggest that the larger observed widths are associated with inhomogeneous broadening due to random dipolar or hyperfine fields. We note that the discrepancy may in part be due to the fact that the relaxation is thermally assisted at temperatures as low as 750 mK and there is evidence for temperature-dependent relaxation even as low as 60 mK [40]; therefore, it seems unlikely that the observed relaxation (especially the present data) can be described in terms of ground-state tunneling. In a calculation that does not incorporate thermal activation, Gunther [28] has calculated the width of the hysteresis steps and concludes that a dynamical transverse magnetic field must be invoked

to account for the discrepancy between his theory and experiment. Prokof'ev and Stamp [26] have argued that the dynamics of hyperfine and dipolar fields must play a role in the relaxation and explicitly calculated how the hyperfine interaction should give rise to Gaussian broadening of the resonance. (In more recent work [31], the same authors offer a calculation of the relaxation at short times and very low temperatures; those results are not relevant to the present study.)

Garanin and Chudnovsky [21] (see also Friedman [34]) have treated the relaxation of Mn_{12} using a model of thermally assisted tunneling in which the tunneling takes place from a level near the top of the barrier and is produced by a static transverse magnetic field. They predict the resonance to be a superposition of Lorentzians, and also invoke inhomogeneous broadening by random fields to account for the broad resonances observed. Fort *et al.* [29] have offered a calculation of the resonance lineshape that fits the data for the zero-field resonance reasonably well. Their calculation is based on the assumption that the tunneling is driven by a fourth-order transverse anisotropy. As the authors note, this approach fails to account for the presence of half of the observed resonances. Luis *et al.* [30] considered a model in which the tunneling is driven by both a transverse anisotropy and a transverse field. This allows all the resonances, although their theory does predict some difference in amplitude between the odd and even resonances that has not been observed. Here, inhomogeneous broadening is invoked to smooth the multiresonant results into a single peak [41].

Some theories have attempted to explain the relaxation of Mn_{12} in terms of mechanisms other than tunneling. Burin, Prokof'ev and Stamp [25] have suggested that the relaxation can occur via dipolar flip-flop processes. This possibility has now been obviated by measurements that show that the resonant phenomenon is substantially unchanged when the Mn_{12} molecules are dispersed in a glassy matrix and thereby have negligible dipole interactions [22]. Very recently, Garg [32] has suggested that the relaxation may be due to a lattice distortion that occurs when levels near the top of the barrier are near resonance. This theory implies a correlation between the width of the resonance and its height and therefore, Garg concludes, the effective barrier is reduced on resonance by about 10 mK; in contrast, experiments indicate that the barrier is reduced by several Kelvin (see above and also [6,39]).

How to interpret the observed lineshape and width remains an open question. One tempting, but unlikely, interpretation is that the lineshape represents the bare (coherent) tunneling rate. If this were the case, then the linewidth would be a sensitive function of applied transverse field, an effect that is not borne out by experiments [5]. Another interpretation is that our results reflect the natural lineshape of the levels that are involved in the tunneling, the width then being a measure of the levels' lifetimes. If we assume that the tunneling is occurring between, say, levels $m = 3$ and $m = -3$, then the observed width of ≈ 250 Oe corresponds to a lifetime $h/g\mu_B(2m)H$ of 2.5 x $10^{-10}s$. While this is typical of spin-lattice relaxation times in many magnetic systems, we note that the measured Arrhenius prefactor $\tau_0(= 2\pi/\omega_0)$ for Mn_{12} is around $10^{-7}s$ and it is this number that is expected [42] to characterize the typical lifetime of excited states in the system. We note this value for τ_0 is anomalously large for superparamagnetic systems, a fact that has been addressed theoretically [42]. It seems, then, that there are three time scales involved in the relaxation process: τ_0, the tunneling time and the time scale corresponding to the resonance width, whatever its meaning.

To summarize, the data presented here leave two mysteries: (i) Why, even in the presence of significant hyperfine fields, is there no apparent inhomogeneous broadening of the resonances?; and (ii) What is the origin of the observed Lorentzian lineshapes? We conjecture that these questions may be related and may be resolved simultaneously. At this point it is clear that the role of the hyperfine interactions in the relaxation of Mn_{12} cannot simply be understood in terms of a random field superimposed on the external field. A more sophisticated model of the interaction of the molecular spin with the nuclear spins seems essential to understand the relaxation mechanism for Mn_{12}.

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[1] J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996); J. R. Friedman, M. P. Sarachik, J. Tejada, J. Maciejewski and R. Ziolo, J. Appl. Phys. **79**, 6031 (1996).

[2] J. M. Hernández, X. X. Zhang, F. Luis, J. Bartolomé, J. Tejada, and R. Ziolo, Europhys. Lett. **35**, 301 (1996).

[3] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature **383**, 145 (1996).

[4] F. Lionti, L. Thomas, R. Ballou, B. Barbara, A. Sulpice, R. Sessoli, and D. Gatteschi, J. Appl. Phys. **81** , 4608 (1997).

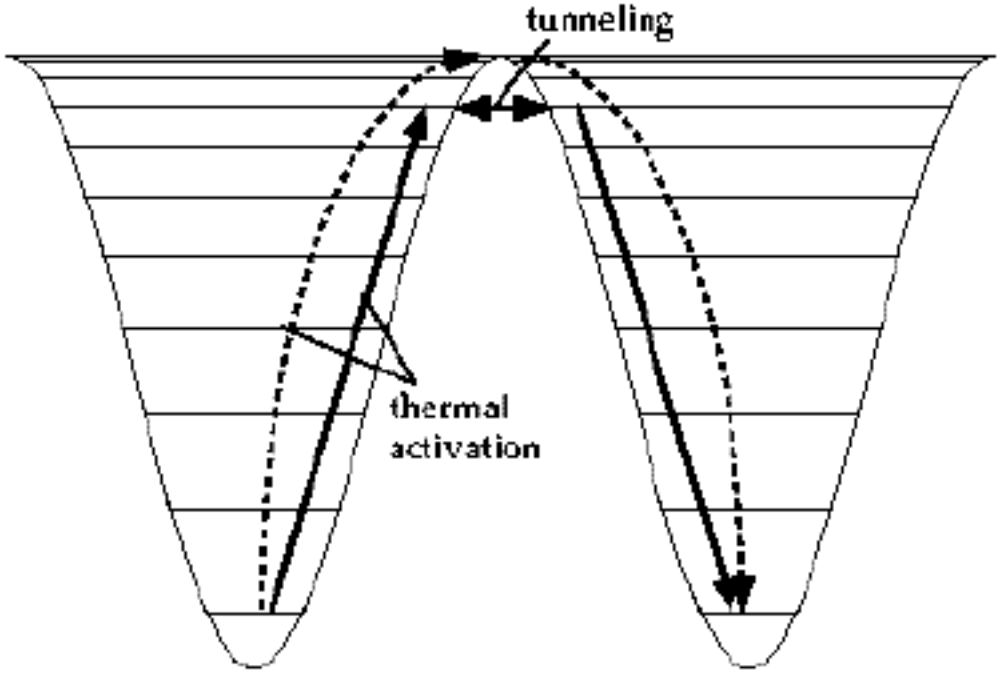
[5] J. R. Friedman, M. P. Sarachik, J. M. Hernández, X. X. Zhang, J. Tejada, E. Molins, and R. Ziolo, J. Appl. Phys. **81**, 3978 (1997).

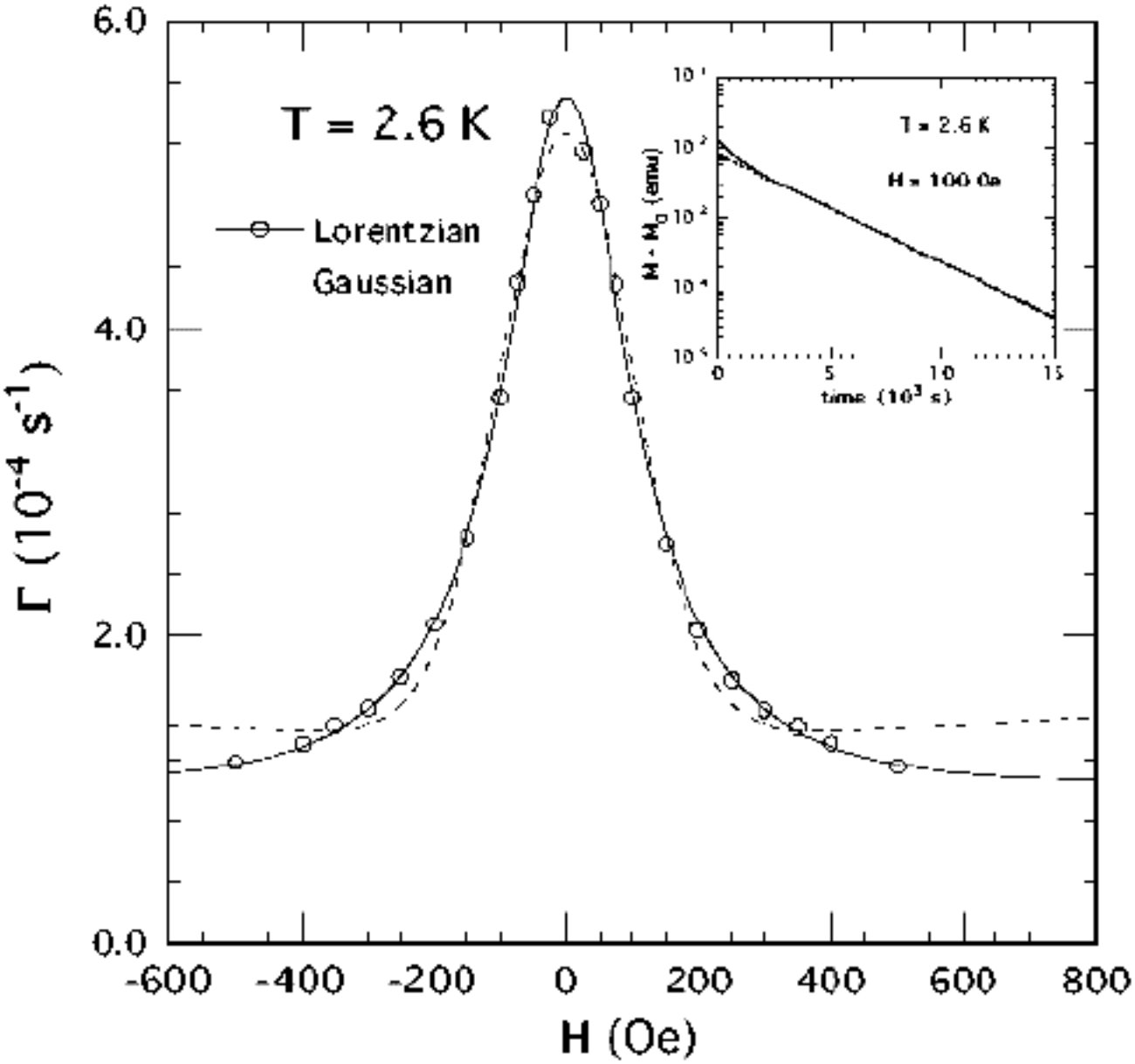
[6] F. Luis, J. Bartolomé, J. F. Fernández, J. Tejada, J. M. Hernández, X. X. Zhang, and R. Ziolo, Phys. Rev. B **55**, 11448 (1997).
[7] S. M. J. Aubin, S. Spagna, H. J. Eppley, R. E. Sager, K. Folting, G. Christou, and D. N. Hendrickson, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **305**, 181 (1997).
[8] C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, Phys. Rev. Lett. **78**, 4645 (1997).
[9] S. M. J. Aubin, N. R. Dilley, M. W. Wemple, M. B. Maple, G. Christou, and D. N. Hendrickson, J. Am. Chem. Soc. **120**, 839 (1998).
[10] D. Ruiz, Z. Sun, B. Albela, K. Folting, J. Ribas, G. Christou, and D. N. Hendrickson, Angew. Chem. Int. Ed. **37**, 300 (1998).
[11] B. Barbara, W. Wernsdorfer, L. C. Sampaio, J. G. Park, C. Paulsen, M. A. Novak, R. Ferré, D. Mailly, R. Sessoli, A. Caneschi, K. Hasselbach, A. Benoit, and L. Thomas, J. Magn. Magn. Mater. **140-144**, 1825 (1995).
[12] M. A. Novak and R. Sessoli, in *Quantum Tunneling of Magnetization*, edited by L. Gunther and B. Barbara (Kluwer, Amsterdam, 1995), p. 171.
[13] J. R. Friedman, Phys. Rev. B **57**, 10291 (1998).
[14] R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, and D. N. Hendrickson, J. Am. Chem. Soc. **115**, 1804 (1993).
[15] A. L. Barra, D. Gatteschi, and R. Sessoli, Phys. Rev. B **56**, 8192 (1997).
[16] S. Hill, J. A. A. J. Perenboom, N. S. Dalal, T. Hathaway, T. Stalcup, and J. S. Brooks, Phys. Rev. Lett. **80**, 2453 (1998).
[17] M. Enz and R. Schilling, J. Phys. C: Solid State Phys. **19** , 1765 (1986).
[18] E. M. Chudnovsky and L. Gunther, Phys. Rev. Lett. 60, 661 (1988); Phys. Rev. B **37**, 9455 (1988).
[19] J. L. van Hemmen and A. Sütö, Europhys. Lett. **1**, 481 (1986); Physica B **141**, 37 (1986).
[20] J. M. Hernández, X. X. Zhang, F. Luis, J. Tejada, J. R. Friedman, M. P. Sarachik, and R. Ziolo, Phys. Rev. B **55**, 5858 (1997).
[21] D. A. Garanin and E. M. Chudnovsky, Phys. Rev. B **56**, 11102 (1997).
[22] A. Caneschi, T. Ohm, C. Paulsen, D. Rovai, C. Sangregorio and R. Sessoli, J. Magn. Magn. Mater. **177-181**, 1330-1336 (1998).
[23] F. Hartmann-Boutron, P. Politi, and J. Villain, Int. J. Mod. Phys. **10**, 2577 (1996).
[24] D. A. Garanin, J. Phys. A: Math. Gen. **24**, L61 (1991).
[25] A. L. Burin, N. V. Prokof'ev, and P. C. E. Stamp, Phys. Rev. Lett. **76**, 3040 (1996).
[26] N. V. Prokof'ev and P. C. E. Stamp, J. Low. Temp. Phys. **104**, 143 (1996).
[27] V. V. Dobrovitski and A. K. Zvezdin, Europhys. Lett. **38** , 377 (1997).
[28] L. Gunther, Europhys. Lett. **39**, 1 (1997).
[29] A. Fort, A. Rettori, J. Villain, D. Gatteschi, and R. Sessoli, Phys. Rev. Lett. **80**, 612 (1998).
[30] F. Luis, J. Bartolomé, and J. F. Fernández, Phys. Rev. B **57**, 505 (1998).
[31] N. V. Prokof'ev and P. C. E. Stamp, Phys. Rev. Lett. **80**, 5794 (1998).
[32] A. Garg, Phys. Rev. Lett. **81**, 1513 (1998).
[33] T. Lis, Acta Cryst. B **36**, 2042 (1980).
[34] J. R. Friedman, Ph.D. thesis, The City University of New York, 1996.
[35] C. Paulsen and J.-G. Park, in *Quantum Tunneling of Magnetization*, edited by L. Gunther and B. Barbara (Kluwer, Amsterdam, 1995), p. 189.
[36] C. Paulsen, J.-G. Park, B. Barbara, R. Sessoli, and A. Caneschi, J. Magn. Magn. Mater. **140-144**, 379 (1995); J. Magn. Magn. Mater. **140-144**, 1891-1892 (1995).
[37] The fits of the long-time tail of the data to an exponential yield negligible statistical errors. The largest identifiable random error in the data presented in Figs 2 and 3 is due to a ≈ 5 Oe uncertainty in the field produced by the superconducting magnet. However, we note there is a large error in the absolute value of the relaxation rate: If we ignore the long-time tail of the relaxation and fit a limited region of the earlier part of the data to an exponential, then the resulting rates can be as much as 20 % larger than those presented. Rates obtained in such a way also fit a Lorentzian function extremely well and so our conclusions remain unchanged.
[38] This form for the nonresonant relaxation rate is valid for $H << H_c$, where $H_c \approx 10$ T is the critical field at which the barrier disappears. Γ_{nonres}, the nonresonant relaxation rate at H = 0, is the only fitting parameter in the expression.
[39] A. M. Gomes, M. A. Novak, R. Sessoli, A. Caneschi, and D. Gatteschi, Phys. Rev. B **57**, 5021 (1998).
[40] J. A. A. J. Perenboom, J. S. Brooks, S. Hill, T. Hathaway, and N. S. Dalal, Phys. Rev. B **58**, 330 (1998).
[41] J. F. Fernández has suggested (1998 March Meeting of the American Physical Society, Los Angeles) that the inhomogeneous broadening of the superposition of two Lorentzian peaks of different widths could give rise to an overall lineshape that resembles a Lorentzian. We believe it is unlikely that such a scheme would yield results that fit a single Lorentzian function with the high fidelity that our data do.
[42] J. Villain, F. Hartmann-Boutron, R. Sessoli and A. Rettori, Europhys. Lett. **27**, 159 (1994).

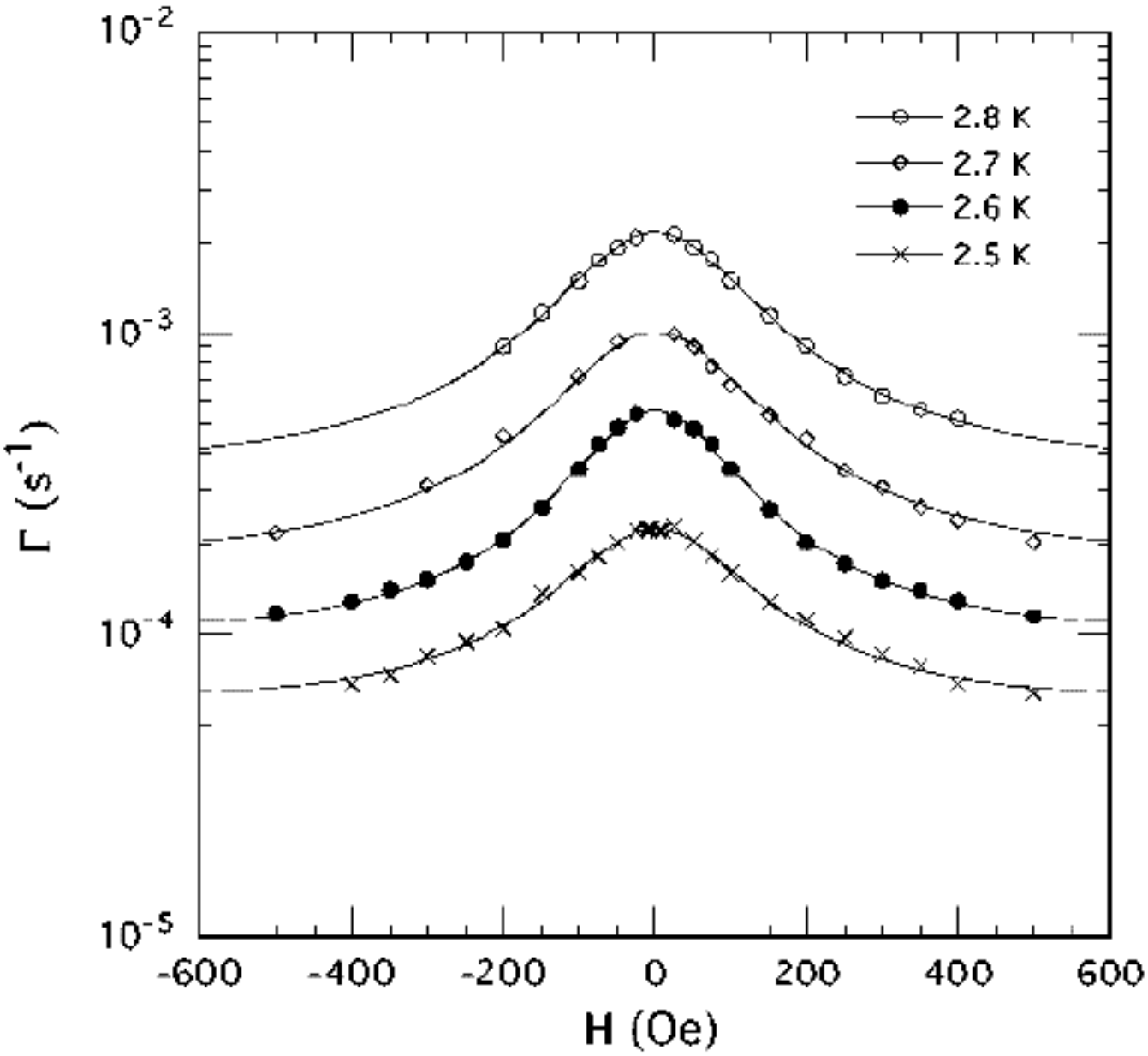
FIG. 1. Double-well potential for the Mn_{12} Acetate, described by Eq. 1 with H = 0. The levels represent different projections of the spin along the z axis (different values of the magnetic quantum number m). For an initial excess population in the left well, the model of thermally assisted resonant tunneling is represented by the solid arrows, while the nonresonant process of simple thermal activation over the classical barrier is represented by the dashed arrows.

FIG. 2. Relaxation rate as a function of applied magnetic field for the zero-field resonance at 2.6 K. Fits to both Lorentzian and Gaussian functions (with the same number of free parameters) are shown. The inset shows the actual magnetization versus time (on a semilogarithmic scale) at 100 Oe. The long-time tail of the relaxation was fit to an exponential (dashed line) to determine the relaxation rate for this field value.

FIG. 3. Semilogarithmic plot of the relaxation rate versus magnetic field for the zero-field resonance at four different temperatures, as indicated. Each data set was fit to a Lorentzian, as shown.


tunneling
thermal
activation


T = 2.6 K
Lorentzian
Gaussian
Γ (10^-4 s^-1)
H (Oe)
6.0
4.0
2.0
0.0
-600
-400
-200
0
200
400
600
800
T = 2.6 K
H = 100 Oe
M - M0 (emu)
time (10^3 s)


10^{-2}
10^{-3}
10^{-4}
10^{-5}
Γ (s^{-1})
2.8 K
2.7 K
2.6 K
2.5 K
-600
-400
-200
0
200
400
600
H (Oe)